SYMPOSIUM L

Recent Developments in Oxide and Metal Epitaxy—Theory and Experiment

April 23 – 26, 2000

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TUTORIAL

ST 1: IN SITU CHARACTERIZATION TECHNIQUES FOR THIN FILM EPITAXY
Sunday, April 23, 2000
1:30 p.m. - 5:00 p.m.
Golden Gate A3 (Marriot)

Thin film epitaxy is integral to many current and emerging technologies and continued progress in solving fundamental issues is critical. In-situ characterization techniques are receiving increasing attention since they offer the possibility to reduce the often unavoidably empirical nature of thin film research and enhance efficiency significantly. Techniques to be covered in the tutorial probe surface and buried interface processes in thin film epitaxy. They include in-situ electron-beam characterization of complex oxide MBE, integrated in-situ time-of-flight ion scattering and recoil spectroscopy, in-situ spectroscopic ellipsometry, x-ray photoelectron spectroscopy and angular electron spectroscopy.

Instructors:
Orlando Anciello, Argonne National Laboratory
Eugene Irene, University of North Carolina
Jim Eckstein, University of Illinois

SESSION 1.1: GROWTH AND DYNAMICS OF METAL FILMS
Chair: Shirley Ching and Andreas K. Schmid
Monday Morning, April 24, 2000
Salon 10/11 (Marriot)

8:30 A.M. #1.1
TAILORING EPITAXIAL TEMPLATES FROM REFRAC\-\Y METAL BUFFERS. C.P. Flynn, University of Illinois, Urbana, IL

Refractory metal buffers such as Ta or W are often used to grow epitaxial films. However, the use of refractory metal buffers can lead to the formation of non-epitaxial films. In this talk, we will discuss the use of refractory metal buffers to grow epitaxial films. We will also discuss the use of refractory metal buffers to grow epitaxial films that are not necessarily refractory in nature. We will also discuss the use of refractory metal buffers to grow epitaxial films that are not necessarily refractory in nature.

The motion of grain boundaries plays a crucial role in determining the properties of thin film materials, especially during use at high temperatures. In spite of this, the motion of grain boundaries is not well understood. A classic example is the Hilsch and Balluffi
classic example is the Hilsch and Balluffi showing a reversible phase transition in an incoherent twin boundary in an amorphous thin film. At about 400K, below this temperature, the phase fact are seen; above this temperature, the twin boundary becomes stable at the length scale of observation. We initially modeled this transition using molecular dynamics. We learned that the grain boundary could move only at a certain energy, that is, the motion occurs by a cooperative motion of four atoms at the junction. Such an excitation transforms a primitive cell of the coincidence site lattice from one orientation to the other thereby moving a portion of the grain boundary. This elementary excitation was mapped onto a simple two-dimensional lattice model incorporating both the topology of the boundary and the energy associated with the transition. With the lattice model, large-scale simulations of the de-faceting transition were performed. The grain boundary structures calculated from the lattice model were in good agreement with the molecular dynamics calculations and with the experimental observations. By examining the roughness, the dislocation, and the specific interface as a function of temperature, we were able to prove that the de-faceting transition is in fact a phase transition and to determine the order of this transition. The lattice model described here is applicable to studies of grain coarsening, and grain mobility in other thin film systems.

9:45 A.M. #1.4
REAL TIME OBSERVATION AND QUANTIFICATION OF DISLOCATIONS IN HICRYSIS. A1 (011) on Si (001). S.A. Stach and U. Dahmen, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, CA; A. Hellman, W. Ni, J. Florando, and E. Leung, Department of Materials Science and Engineering, Stanford University, Stanford, CA; A. Schwarzenbach, Department of Materials Science and Engineering, Brown University, Providence, RI

The mechanical properties of thin metallic films on silicon have been a topic of intense study over the past several decades. Various mechanical testing techniques, including wafer curvature, nanoindentation and microbeam bending, have been developed to elucidate the mechanisms by which strains are relaxed during thermal cycling of these structures. In this work, we focus on the strain relaxation behavior of a model heterosystolic metal film on silicon substrate system. Deposition of aluminum onto silicon at a substrate temperature of 280°C results in the formation of a mixed crystal structure consisting of two variants of [111] Thermoelastic stress. By subjecting these structures to thermal cycles within the electron lens of a transmission electron microscope, we are able to observe directly the nucleation and motion of dislocations within the aluminum grains via diffraction contrast imaging. Upon cooling from an annealing temperature of 450°C, we find that pre-existing dislocations initially move slowly, within the plane of the film, by a combination of stress-assisted dislocation climb and cross-slip. This results in little relaxation of the film. However, dislocation nucleation and glide is observed to occur along the (111) 1/2 < 110 > slip systems in a dynamic burst. Subsequent dislocation motion upon further cooling is strongly hindered by dislocation interaction. This simplicity of the crystal microstructure in these films permits direct correlation of our observations of dislocation motion with quantitative...
measurements of epitaxial strain and theoretical models of dislocation behavior. We will compare and contrast our observations in these model bicrystal aluminum samples with similar observations we have made in large-grained polycrystalline samples, thereby shedding light on the mechanisms by which dislocations mediate plasticity in metal films on silicon.

10:30 A.M. *L1.5*

SPATIAL CORRELATIONS IN GROWING FILMS. M.C. Bartelt, Sandia National Laboratories, Livermore, CA.

Detailed analyses of non-equilibrium lattice-gas models of island nucleation and growth during film deposition or etching have been invaluable in elucidating basic issues in nucleation theory, deviations from mean-field predictions, and experimental observations. Particularly interesting and useful is the behavior of correlations in the adlayer which develop during island formation. Spatial non-uniformities in the density, n, of diffusing adspecies determine island nucleation and growth rates. In particular, a strong dependence of the population of island pairs at separations smaller than the average follows from depletion in n near islands. This feature delays island percolation. In addition, island-free areas surrounding islands are larger for bigger islands, reflecting strong correlations between island size and separation. Through the island size dependence of the island capture numbers, these correlations control the shape of the island size distribution [1]. When incorporated into rate-equation descriptions, they recover the exact form of the scaling function for the island size distribution [1, 2].

For competition with results from many and long studies [2]. For example, for Co islands on Ru(0001), I show how the rate and direction of capture of additionally deposited Co atoms reflect the local environment of individual islands, as predicted by simulation [2].

11:00 A.M. *L1.6*

RATE EQUATIONS AND EFFECTIVE CAPTURE NUMBERS. F. Gilboa, C. Raisch, UCLA, Dept. of Mathematics and HRL Laboratories, Malibu, CA; S. Chen, R. Cofield, UCLA, Dept. of Mathematics; M. Gyure, HRL Laboratories, Malibu, CA.

The mean field rate equations that form the basis of nucleation theory have been used for over 25 years to study epitaxial growth. One problem in using rate equations is that the functional form of the capture coefficients for islands of size S is not known. Several approximations for σ are given in the literature, while some correctly reproduce averaged quantities, none of these approaches has given the experimentally observed scaling of the island size distribution. In this paper, we show that the problem is the correct interpretation of the meaning of the capture numbers. We propose a new definition for these coefficients and compute them numerically using the level-set formalism. The main idea is that σ depends on the capture efficiency of all sizes of smaller than S. We then show for the first time that incorporating rate equations gives the correct scaling of the island size distribution.

11:15 A.M. *L1.7*

FILM RIPENING BY RANDOM EXCHANGE OF ADATOMS. S.J. Koh, G. Ehrlich, Univ of Illinois at Urbana-Champaign, Materials Research Laboratory and Dept of Materials Science and Engineering, Urbana, IL.

In the later stages of island growth on a surface, larger islands may grow at the expense of smaller islands, in a process known as Ostwald Ripening. The driving force for this is the higher chemical potential of smaller islands, which produces higher adatom concentrations and results in a net flow of adatoms from smaller to larger islands. Here, we wish to report that ripening can also occur by a random exchange of adatoms between the islands, without any chemical potential difference. This phenomenon has been observed in a model system: one-dimensional clusters of Ir on W(110). Two parallel, one-dimensional Ir chains are prepared on the W(110) surface, which is then heated to 900°C. The rate of individual atoms in the two Ir clusters is monitored with a field ion microscope. The length of each chain is observed to fluctuate as adatoms are exchanged between the two chains. Occasionally the smaller chain is found to grow, consuming the larger surface chain. Detailed analysis shows that the exchange of adatoms between two chains is a random process. Analogous events are expected to contribute to the usual Ostwald Ripening, especially when there is a difference in the chemical potential of participating particles is small. (Supported by the US Department of Energy under Grant No. DEFG02-92ER-14520)

11:30 A.M. *L1.8*

MODELING OF METAL (100) HOMEOPITAXIAL FILM GROWTH AT VERY LOW TEMPERATURES. K.J. Capesius, C.R. Stoldt, P.A. Thiel and J.W. Evans, Iowa State University, Ames, IA.

In late 1980's, unexpectedly smooth growth was observed in metal (100) homoepitaxy around 100 K, where terrace diffusion is inoperative. After some initial speculation on the role of transient mobility, this smooth growth was finally attributed to downward funneling of atoms deposited at step edges to lower four-fold hollow adsorption sites. Recent VI-STM studies for Ag/Agl(100) reveal a more complicated picture. In particular, a strong dependence of the population of island pairs at separations smaller than the average follows from depletion in n near islands. This feature delays island percolation. In addition, island-free areas surrounding islands are larger for bigger islands, reflecting strong correlations between island size and separation. Through the island size dependence of the island capture numbers, these correlations control the shape of the island size distribution [1]. When incorporated into rate-equation descriptions, they recover the exact form of the scaling function for the island size distribution [1, 2], thus overcoming longstanding limitations of traditional mean-field treatments. I will illustrate several of these results with experiments and simulations [3].

For example, for Co islands on Ru(0001), I show how the rate and direction of capture of additionally deposited Co atoms reflect the local environment of individual islands, as predicted by simulation [2].

11:45 A.M. *L1.9*

THE LEVEL-SET METHOD FOR MODELING EPITAXIAL GROWTH. C. Raisch and M.F. Gyure, HRL Laboratories, Malibu, CA; R. Cofield, S. Chen, M. Kurig, B. Merriman, S. Osher and M. Wheeler, UCLA, Los Angeles, CA; D.D. Vvedensky, Imperial College, London, UNITED KINGDOM.

We develop an island dynamics model that employs the level-set technique to describe epitaxial growth. The surface morphology is described by defining the location of the lowest energy of the so-called level-set function. Islands are nucleated on the surface and their boundaries are moved at rates that are determined by the adatom density, which is obtained from solving the diffusion equation. Several island size distributions and the boundary evolution of the monolayer aggregation regime are compared with those obtained from a kinetic Monte Carlo (KMC) simulation for irreversible as well as reversible aggregation. Excellent agreement is obtained. We identify spatial fluctuations in the mobility of islands as the cause for the size selectivity of the growth law. We also show that the level-set method can naturally be extended to multilayer growth; here, the set ψ = n corresponds to the nth layer. Roughening and Corrowing of the surface will be discussed. In particular, we will study the evolution of the step density, which is related to the RHED signal in experiment. A qualitative and quantitative comparison to KMC simulations will be given.

SESSION L2: STRUCTURE AND OXIDATION OF METAL FILMS AND SURFACES

Chair: Robin F. C. Farrow and C. Peter Pym

Monday Afternoon, April 24, 2000

Salon 10/11 (Marriott)

1:30 PM L2.1


In most prior surface science studies, it has been assumed that total exposure, rather than both pressure and time as independent variables, controls the types of adsorption structures formed. However, the potential importance of deposition pressure has recently been suggested in a study of the kinetics of the low pressure adsorption of oxygen on W110) using photoelectron spectroscopy and desorption

We have used ultrahigh vacuum scanning tunneling microscopy (STM) to examine the adsorbate structures and the coverage dependence of oxygen on W110) as a function of the deposition pressure and for room temperature exposures. For the same total adsorbate exposure at 10-10 torr, the oxygen coverage at room temperature is 0.4 monolayer. The oxygen coverage decreases to 0.2 monolayer at 10-11 torr. This is attributed to the interaction between the adsorbate layer and the surface. Adsorbate layer stability decreases with decreasing pressure.
images vary only from 13-17% of a monolayer (ML) for this exposure range. In comparison, STM images of the surface resulting from intermetallic compound formation (1100) show uniform domains of sizes approximately 30 x 50 Å with adlayer coverages of 1.530% ML. Higher pressure deposition (10^-7 Torr) for total exposures of 3 to 6 L yields structures with the well-known LEED patterns (1 x 2) and (2 x 2) and the STM images of these structures clearly show large well-ordered domains of these different types. The possible kinetic mechanisms of the adsorption leading to this strong pressure dependence will be discussed. Additional experiments to include the temperature of desorption and of these kinetic mechanisms are in progress.


1:45 PM #1.2.2

HETEROPTAXY: THE MISSING LINK BETWEEN SURFACE CHEMISTRY AND DIHYDRO CORROSION. Judith Yang, University of Pittsburgh, Dept. of Materials Science and Engineering, Pittsburgh, PA.

Understanding the oxidation process is of fundamental and practical interest because thin film growth, such as ferroelectric, corrosion, passivation, and some catalysis involve oxidation. However, there exists a surprising paucity of information concerning the transient oxidation stages, from the formation of the initial oxide to the growth of the thermodynamically stable oxide. To bridge this gap, we are visualizing the initial oxidation of Cu(001) by in situ ultra-high vacuum (UHV) transmission electron microscopy (TEM). Oxidation potentially involving surface diffusion, nucleation, and growth, which is strikingly similar to epitaxial deposition. We wish to apply and extend these theories of heteroepitaxy to explain the initial oxidation stage on model metal systems. The nucleation and growth of Cu-O due to oxidation of Cu films were monitored at various temperatures and oxidizing environments, including dry oxygen and water vapor, up to atmospheric pressures. Based on this data, we have developed a semi-empirical model of the initial oxidation stage where the dominant mechanism is oxygen diffusion on the Cu surface. We have compared our experimental data with nucleation rate theory, where we find that a density of nucleation rate that quantitatively predicts the oxide nucleation behavior with respect to temperature and pressure. For real-world conditions, we have also focused on passivation film formation due to oxidation in air at ambient temperature.

The chemical theory of Cabrera-Mott describes passivation film formation on metals, where they predicted that this film grows as a uniform layer due to a field-enhanced ionic transport mechanism. Here we present experimental evidence that the passivation film nucleates and grows as oxide islands, not as a uniform layer. We propose an alternative phenomenological theory to describe passivation film formation, based on island growth followed by coalescence.

2:15 PM L2.3

A NOVEL METHOD FOR TRUE WORK FUNCTION DETERMINATION OF METAL SURFACES BY COMBINED KELVIN PROBE, PHOTOELASTIC EFFECT MEASUREMENTS. Bert Lijek, Inan Din, Konrad Richter, Konrad Ronchetti, Uwe Petermann, Robert Gordon Univ., Dept. of Applied Physics, Aberdeen, UNITED KINGDOM.

We have developed a novel method for in-situ measurements of the true work function (ϕ) of metal surfaces by combined ultra-high vacuum compatible Kelvin Probe and photoelastic effect measurements. The work function is an extremely sensitive parameter of surface conditions and can be used to study oxidation and thin film growth on metal surfaces [1]. For example, the increase in ϕ due to oxidation of polycrystalline rhodium at 800 K is 1.9 eV. The Kelvin Probe measures local work function differences between a conducting sample and a reference tip in a non-contact, truly non-invasive way over a wide temperature range. However, it is an inherently relative technique and does not provide an absolute work function if the work function of the reference tip is not known. We have developed a method to measure ϕ with the Kelvin Probe using the photoelastic effect, thus combining the advantages of both methods to provide the absolute work function of the sample surface. We demonstrate the application of our method by determining the work functions of evaporated thin films of rhodium and follow the oxidation kinetics of rhodium with oxygen exposure. The extended Kelvin Probe method therefore has potential applications as a characterization tool for thin film epitaxy, semiconductor etching, and surface science.


3:00 PM L2.4

ATOMIC MECHANISMS OF SURFACE ALLOY FORMATION. Andreas Schmidt, Sandia National Laboratories, Livermore, CA.

Metals that do not form bulk alloys can often produce stable mixed phases at surfaces. This short communication describes the growth of a misfitting alloy at the surface, this talk will focus on the importance of surface adatoms and dislocations governing intermixing dynamics. Our experimental method is an adaptation of the classical approach of mixing diffusion-repulsive interdiffusion. We show that diffusion across linear interfaces separating monolayer films of two different metals are measured by scanning tunneling microscopy. We find that the interdiffusion of Co and Cu in monolayer films on the Ru(0001) surface occurs through the combination of adatom surface diffusion and exchange of adatoms with atoms in the films. Further, the importance of dislocations in thin films is addressed by probing their influence on interdiffusion. As a test case, we studied intermixing between dislocated monolayer regions of Au adjacent to pseudomorphic monolayer regions of Pt on Ru(0001). Dramatic interface motion and pronounced anisotropy of interdiffusion were found. We show how these unusual effects result from the dynamic behavior of dislocations present in the films and how they can be incorporated into the interface diffusion equation.

3:30 PM #1.2.5


The angular dependent magnetoresistance, magnetization, and growth of epitaxial Fe(001)/Al2O3 self-assembled lateral multilayers (SALMs) have been examined in order to explore the interplay of structure and magnetism. SALMs consist of thin film alloys of immiscible metals grown on Mo[110]/Al2O3(11-20) template layers and display a unique form of compositional ordering not observed in the bulk. These structures are observed to form a compositionally ordered alloy of alternating, contiguous strips of Fe (or Co) and Ag with the long axis of the strip coinciding with the Mo[001] direction in the plane of the substrate. The average stripe periods are on the order of 1.8 to 3.6 nm along the Mo[110] parallel to the Mo[001] direction. The low temperature anisotropic magnetoresistance (AMR) and low field magnetoresistance (MR) are examined as a function of field angle for two nearly orthogonal current directions equivalent to the CPP and CIP configurations. The SALM structures are observed to display a significant AMR of nearly 100% for the entire structure. Furthermore, an pronounced MR is observed with a maximum ΔR/R of 0.88% (~29% in the active layer) at 2.7 K.


4:00 PM L2.6

THICKNESS-DEPENDENT TETRAHEDRAL RELAXATION IN IRON EPITAXIAL Fe/Pd MULTILAYER FILMS. Ch. Mühle, H. Mühlbauer, T. Steffen, B. Rellinghaus and G. Dambach, Experimentelles Thermosynthese-Institut, Universität Kassel, Germany.

The preparation of magnetic multilayers (ML) with iron is of interest, since they allow for metastable single-domain magnetic states (α-Fe), which is expected to undergo a volume-mediated change from antiferromagnetic order with low magnetic moment (LM) to ferromagnetic order with high magnetic moment (HM). Recently, we have shown that in polycrystalline Fe/Pd multilayers grown up to 10 monolayers in the former phase exhibiting a moment of 2.7μB, whereas for thicker Fe layers, the bcc structure (α-Fe) becomes more stable and the moment is reduced to the bulk value of 2.2μB [1]. To shed more light on the structural transition of Fe layer growth, we have prepared epitaxially grown Fe/Pd MLs on single-crystal iron substrates and, in a second step, on the Fe/Pd substrates. We have measured the growth in-situ via RHEED and STM. In addition, we have prepared Fe/Pd MLs on (110) silicon and (HR) TEM on cross section samples. We find that epitaxy is preserved throughout the film as n = 32 periods within the ML stacks, though STM images clearly show a significant roughness of the surfaces. RHEED proves the 3-Dimensional (3-D) epitaxy of silicon samples, whereas Fe/Pd layers, the latter is successively tetragonally compressed along the growth direction, whereas the in-plane lattice constant remains constant. The Fe atomic volume is thereby decreasing the volume from that of bulk Fe. The effect on the magnetic properties of the samples is discussed.

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4:15 PM L1.2.7
THE ROLE OF STRAIN IN THIN FILM ALLOY THERMO-
DYNAMICS: COMPARISON BETWEEN ALLOYING AND
DELOCALIZATION. Proctor, T. Department of Physics,
University of Oxford, Oxford, UK. V. Hwang, Department of
Physics, Davis, CA; Andrew K. Schmid, N.C. Bartelt, V. Oudalov, A. M. Asta, J. J. Hoyt, Sandia National Labs, CA; S. Chiang, UC Davis, Department of Physics, Davis, CA; R. Q. Hwang, Sandia National Labs, CA.

It has long been known that the structure of materials in thin film configurations can differ tremendously from their bulk phase. This is particularly true of alloy films. In particular, it has recently been shown that strain mismatch between the substrate and film can lead to the formation of novel alloys that do not exist in the bulk. A prototypical example is the system of monolayer Ag/Co films grown on Ru(0001). In the bulk, Ag and Co are immiscible. However, on the Ru surface, alloy phases of finite stoichiometries are formed. Phase segregation between a pure Ag phase containing dislocations and a pseudomorphically strained Co$_2$Ag$_6$ phase has been found. The driving force for segregation is the competition between two strain relief mechanisms. In the pure Ag phase, strain is relieved by dislocation formation. In the Co-rich alloy phase, strain is relieved by forming neighboring regions of both Ag and Co which experience opposite signed strain relative to the Ru substrate. This has been predicted by first principles calculations for pseudomorphic films. These predictions have been quantitatively compared to the experiment by measurements of the atomic strain in the interface between the Ag and Co regions in the alloy phase.

4:30 PM L1.2.8
ELABORATION OF SINGLE CRYSTALLINE Au/Ni$_{50}$Fe$_{20}$/Cux/
Ni$_{50}$Fe$_{20}$/Ni(111) SPIN VALVES. Antoine Barbier, Christian
Monforti, Stéphane Gaubert, Gaëtan Guittard, Département de
Recherche Fondamentale sur la Magnétisme Condensé, Grenoble,
FRANCE.

NiO is a highly corrosion-resistant antiferromagnet. NiO(111)-based spin valves are interesting field sensors which could be used in hard drive read-heads, permanent magnetic memories as well as in harsh environments applications. Since spin valves are complex structures, the understanding of the role of the interface (or exchange interaction) with respect to the general behavior of NiO is of high interest. We will show that high quality NiO(111) single crystal polar surfaces can be obtained. They are always stabilized by a (2x2) reconstruction. These surfaces allowed the investigation of the growth of permalloy (Py, Ni$_x$(Fe$_{94}$)$_x$) on NiO(111), with respect to the growth temperature, by grazing incidence X-ray diffraction. This technique offers a major advantage: it is not limited by the change build-up: the experiments were performed at the European Synchrotron Radiation Facility in Grenoble, France. The Py layer built on the NiO(111) single crystal behaves like a hard magnetic material because of the interfacial exchange coupling. Growth conditions of the whole spin valve (in which the second Py layer is the sensing soft magnetic layer) in epitaxial growth lines of different temperature regimes were performed. High resolution TEM allowed understanding how deviations from the epitaxial growth regime prevent the onset of the GMR. These results open the possibility to study fully epitaxial spin-valves in order to understand better the exchange coupling occurring at ferromagnet/antiferromagnet interfaces.

4:45 PM L1.2.9
INTERFACIAL ENERGIES OF METALS ON OXIDES BY STM: Ag
AND Cu ON (1x1)-TiO$_2$(110). S.M. Seutner, M.C. Bartelt, R.Q.
Hwang, K.F. McHenry, Sandia National Laboratories, Livermore, CA; D.A. Chelnokov, Chemistry and Biochemistry, Univ. of South Carolina, Columbia, SC; D.R. Jennison, Sandia National Laboratories, Albuquerque, NM.

An important issue in heteroepitaxy and materials-joining technologies is the interfacial energy between overlayer and substrate. For example, the smaller the interfacial energy, the stronger the adhesion at the interface. For many metal-on-oxide systems, interfacial energies have been derived. We demonstrate that scanning tunneling microscopy (STM) has been used to measure interfacial energies of Ag and Cu films on TiO$_2$(110) surfaces. Monolayer coverages (0.1 to 0.3 monolayers) of Ag or Cu were first evaporated on room temperature (RT) or on temperatures up to ultrahigh vacuum (UHV). The sample was then annealed at 850K for 1 minute to form equilibrium, faceted metal islands with diameters of 10 to 15 nm and heights of 1 to 2 nm, as observed by STM at RT in UHV. More Ag could not be obtained with higher substrate temperature anneals. From STM height profiles of the islands, a Wilk analysis was used to estimate interfacial energies, assuming Cu and Ag islands have top [111] facets with surface energies of ~2 J/m$^2$ and ~1 J/m$^2$, respectively [1], and the TiO$_2$(110) substrate has a surface energy of 0.7 J/m$^2$. [2] We find unexpectedly low values of 0.4±0.2, 0.2 J/m$^2$ for Cu/TiO$_2$(110) and 0.5±0.2 J/m$^2$ for Ag/TiO$_2$(110), as compared to other metal-on-oxide systems. These values are close to predictions from first-principles density functional theory within the generalized gradient approximation, using a large supercell to approximate an incommensurate interface [3]. We also discuss the nature of such strong adhesion of Cu and Ag on (1x1)-TiO$_2$(110).


SESSION L2: IN SITU STUDIES OF COMPLEX
OXIDE GROWTH ON OXIDE SUBSTRATES
CHairs: Rodney McKee and Mark Yeaden
Tuesday Morning, April 25, 2000
Salon 10/11 (Marriott)

8:30 AM L2.1
THE IMPORTANCE OF IN SITU MONITORS IN THE
PREPARATION OF LAYERED OXIDE HETEROSTRUCTURES
BY REACTIVE MBE. D.G. Schowalter, J.H. Hovel.
Department of Materials Science and Engineering, Penn State
University, University Park, PA; W. Tian, X. Q. Pan, Department of
Materials Science and Engineering, University of Michigan, Ann
Arbor, MI; G.W. Brown, M.E. Hawley, Materials Science and
Technology Division, Los Alamos National Laboratory, Los Alamos,
NM.

Molecular beam epitaxy (MBE) has achieved unparalleled control in the growth of semiconductors at the nanometer level; its use for the integration of oxides with similar nanoscale customizations appears promising. This talk will describe the use of reactive MBE to synthesize layered oxide heterostructures including new compounds and metastable superlattices. We will illustrate how combinations of in situ RHEED, atomic absorption spectroscopy (AA), a quartz crystal microbalance (QCM), and adsorption-controlled growth conditions have allowed the controlled growth of Sr$_2$TiO$_4$, SrTiO$_3$, Sr$_2$RuO$_4$, Sr$_2$IrO$_4$, and Sr$_2$CoO$_3$ superlattices. The controlled synthesis of such layered oxide heterostructures offers great potential for tailoring the superconducting, ferroelectric, and dielectric properties of these materials. Structural and electrical characterization will be presented including in situ RHEED, 4-circle x-ray diffraction analysis, AFM, and high-resolution TEM images. Comparisons between the growth of compound semiconductors and oxides by MBE will be made. The importance of the underlying substrate and its preparation will be highlighted.

9:00 AM L2.2
OXIDATION KINETICS DURING OXIDE EPITAXY STUDIED BY
AN OBLIQUE-INCIDENCE OPTICAL REFLECTIVITY
DIFFERENCE TECHNIQUE. Xu X. Xi, Q. Li, S. Sheng, M. J.
Jennison, Materials and Devices Division, University of California,
Dept. of Physics, Davis, CA; Weidong Si, X.X. Xi, Q. Li, Penn State
University, Dept. of Physics, University Park, PA; Qidu
Jiang, M.G. Mediaco, University of Houston, Dept. of Physics,
Houston, TX; Guo-zhen Yang, Huihui Lu, Fan Chen, Zheng-hao Chen, Institute of
Physique, Chinese Academy of Sciences (CAS), Beijing, PR CHINA.

We studied oxidation kinetics in the epitaxy of SrTiO$_3$, Sr$_2$O$_3$, SrTi$_2$O$_5$, Sr$_2$RuO$_4$, Sr$_2$IrO$_4$, and Sr$_2$CoO$_3$ (SBO) on SrTiO$_3$ (001) during pulsed laser deposition. By monitoring the linear optical response of these deposited monolayer oxide with an oblique-incidence reflectivity difference technique, we were able to determine the kinetics of oxidation of the monolayer with the ambient oxygen. We find the kinetics to vary from oxide to oxide over a wide range. As a result, epitaxial oxide films grown at a rate of a fraction of monolayer per second can easily have a high degree of oxygen deficiency relative to the state of the thermodynamic equilibrium under the growth conditions. We also found that, at sufficiently high temperatures, the oxygen in the SrTiO$_3$(001) substrate is mobile enough to move to the surface and oxidizes the more oxygen-deficient oxide overlayer, even in the presence of ambient oxygen. We present both the experiment and a simple theoretical model that describes the temperature and pressure dependence of the oxidation.

9:15 AM L2.3
ATOMIC LAYER CONTROL OF EPITAXIAL Sr$_2$O$_3$, SrTiO$_3$, Sr$_2$RuO$_4$ HETEROSTRUCTURES ON TiO$_2$-TERMINATED [001] SrTiO$_3$ SUBSTRATES BY IN SITU HIGH PRESSURE RHEED.
Atomic scale control of epitaxy in complex oxide heterostructures is very important for the fabrication of novel devices and the understanding of solid state phenomena. We have grown SrRuO$_3$/SrTiO$_3$-based heterostructures on perfect SrTiO$_3$-terminated (001) SrTiO$_3$ substrates using pulsed laser deposition including in-situ high pressure RHEED. SrRuO$_3$ is an ideal system to study the heteroepitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. SrRuO$_3$ is a conductive ferromagnetic oxide with a lattice parameter of 3.93 Å, i.e., a lattice mismatch with [001] SrTiO$_3$ substrates of 0.64%. AFM studies revealed that the surface morphology of each layer is extremely smooth with a layer-by-layer height growth without any step bunching. Furthermore, sharp 0th-order Bragg reflections in the RHEED pattern and very low diffuse background intensity confirm the perfect crystalline surface. Our RHEED intensity data and AFM images suggest that the SrRuO$_3$ films on SrTiO$_3$ substrate grow in the step-flow mode with a transition from 2-dimensional layer-by-layer mode into step-flow mode after covering one monolayer of SrRuO$_3$. In contrast, the SrTiO$_3$ films on SrRuO$_3$ grow in the two-dimensional layer-by-layer mode. Such an atomic scale control of the interfaces and barrier layers in ferromagnetic oxide [FML-FM] triglycerine layers allows for quantitative analysis of spin-polarized transport across the ferromagnetic oxide [FM-LFM] triglycerine junction interface, which will be discussed.

4:05 AM L3.4
TIME-RESOLVED STUDIES OF SrTiO$_3$ HOMOEPITAXY BY SYNCHROTRON X-RAY SURFACE DIFFRACTION
G. Eres, J. E. Budni, B. C. Larson, D. H. Longe, C. M. Rouleau, M. J. Tischler, and M. Yoon, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; and Zehui’s UNCD, University of Illinois at Urbana-Champaign, Urbana, IL.

The ability to monitor the evolution of atomic scale surface structure in real time facilitates the fundamental studies of the mechanisms that govern thin film growth processes. The high brilliance of third-generation synchrotron light sources provides dramatically increased count rates that enable time dependent measurements of the interference between the substrate and the over layer at the weakly scattering crystal truncation rods (CTR). In this paper we describe application of synchrotron x-ray surface diffraction in time resolved studies of SrTiO$_3$ homoepitaxy by pulsed laser deposition. The intermittent nature of the laser ablation process allows measurements of the surface structure during and after the arrival of the ablation plume. The evolution of the crystalline structure was deduced from measurements of in-plane reflections ($h,k,l$) and specular ($h,k,l=0$) CTR reflections. The in-plane measurements provide information about the incorporation of atoms parallel to the surface, and the specular reflections provide information about their relative location perpendicular to the surface. The experimental results will be compared with Monte Carlo studies addressing the observed time dependence in terms of the surface disorder resulting from the arriving plume, and the subsequent recovery governed by the balance between diffusion and ordering kinetics.

SESSION L4: EPITAXIAL GROWTH OF OXIDES ON OXIDE SUBSTRATES
Chairs: Jerry Hallmark and Mark Yoden
Tuesday, April 25, 2000
Salon 10/11 (Marriott)

10:30 AM L4.1
GROWTH DEPENDENT FIELD-DEPENDENT MAGNETIC DOMAIN STRUCTURES IN La$_{0.67}$Sr$_{0.33}$MnO$_3$ THIN FILMS
M.E. Hawley, G.W. Brown, P.C. Yashar and C. Kwon, Los Alamos National Lab., Los Alamos, NM

Maze- and bubble-like magnetic domain structures have been observed under ambient conditions in La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) films by magnetic force microscopy (MFM) for films grown on a compressive [LaAlO$_3$] lattice mismatched substrate. In this study, we have examined films grown at 550°C to 800°C by pulsed-laser deposition by scanning tunneling and magnetic force microscopy to obtain both magnetic and topographic images. Grain size was found to correlate with coercivity measured by VSM.

Substrate-induced stress and growth related microstructure in this soft magnetic material was found to be responsible for the appearance and nature of magnetic structures. The stress was reflected in distortions to the unit cell measured by x-ray diffraction. In addition, the magnetic structures were found to be a function of initial magnetic field strength. Also, films nominally grown under the same conditions, possessed subtle differences in domain structure and wall spacing, the latter due in part to differences in film thickness. As the field was increased, the maze-like structures transformed into stripe domains with reduced out-of-plane magnetization and decreased wall spacing. These observations were consistent with parallel rather than antiparallel alignment of in-plane spin polarization. After removal of the field, the stripe-like domains remained but the wall spacing and the polarization component returned to the original value. For one 800°C the field-dependent magnetic structures were correlated to VSM data. The changes in the magnetic structure correlated directly with the nonlinear hysteretic magnetic behavior. Wall motion was responsible for the rounding in the VSM curves. A comparison was made between the form film and one capped by a thin insulating layer where the domains were pinned in the remanent state.

10:45 AM L4.2
EPITAXIAL TiN OXIDE THIN FILMS ON THE SAPPHIRE SUBSTRATE BY ULTRAFAST LASER ABLATION DEPOSITION
X. Q. Pan and L. Fu, Dept. of Materials Sci. & Eng., University of Michigan, Ann Arbor, MI; P. Pronko, Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI.

Owing to its high sensitivity to small concentrations of chemical gases as well as high chemical and mechanical stability, SnO$_2$ with the rutile structure is widely used as a base material in chemical sensors. In particular, SnO$_2$ thin films have recently drawn much interest because of their potential application in microsensor devices. In this paper we report our experimental results on the synthesis and characterization of SnO$_2$ epitaxial thin films on sapphire substrates.

The SnO$_2$ thin films were deposited on the sapphire substrates with different surface orientations by a pulsed laser deposition using a femtosecond laser. The energy distribution of ions and neutral atoms in the ablation plume is analyzed using an ion energy spectrometer. The ion spectra provide information on the Sn/O ratio of the ablation plume, prior to its being mixed with the background discharge oxygen gas. The on-line plasma and plume diagnostics also gives information on how isothermally regulated the plume remains as it moves toward the substrate. Thin film microstructures were investigated by both x-ray diffraction and transmission electron microscopy techniques. It was found that the SnO$_2$ thin films grown on the (10-12) surface of sapphire substrate are epitaxial, single crystal, while those films on the (001) surface of sapphire consist of textured structures with both (101) and (200) oriented grains. The epitaxial growth mechanisms of SnO$_2$ thin film will be discussed based on the analysis of the ablation plume - substrate interaction and the film substrate lattice mismatch.

11:00 AM L4.3
Abstract Withdrawn.

11:15 AM L4.4
THE EFFECT OF MgO BUFFER ON THE EPITAXIAL GROWTH OF ZnO ON Al$_2$O$_3$ (0001)
Yefei Chen, Hong-ju Ko, Soon-ku Hong, Takanari Hanaoka and Takanari Yogo, Institute for Materials Research, Tohoku University, Sendai, Japan; Yujiro Segawa and Photon Dynamics Research Center, Institute for Physical and Chemical Research, Sendai, Japan.

Among wide bandgap semiconductors, ZnO is characterized by its direct bandgap in UV region, the strongest bond strength among II-VI semiconductors and very high exciton binding energy of 60 meV. Recent studies showed that the extremely stable excitons, which survive well at room temperature, enable ZnO a promising material for applications to low threshold excitonic lasers. To date, because of the absence of suitable substrate materials, main efforts on ZnO epitaxial growth have been concentrated on Al$_2$O$_3$ (0001) substrate. However, because of the lattice and thermal mismatch, the ZnO films grown on Al$_2$O$_3$ (0001) showed poor surface morphology and crystal quality. In the present paper, we demonstrate how to improve surface morphology and crystal quality of ZnO epilayer by using a thin MgO buffer. Since MgO itself is an II-VI oxide compound, the growth is carried out in the same chamber for growing ZnO without inter-contamination problem. Also there is no additional problem in device design caused by a MgO layer, which is completely transparent at the wavelength of ZnO. The ZnO films grown on widely used low cost sapphire substrate by plasma assisted molecular beam epitaxy. The thin MgO buffer is very effective on the improvement of surface morphology during initial growth stage, which eventually leads to a atomically smooth surface. As the surface reconstruction of ZnO is observed and reflection high-energy electron diffraction intensity oscillation is recorded on ZnO, which indicates the achievement of layer-by-layer growth. Structural analysis indicated that the twin defect with a 30° in-plane crystal orientation mis-aligning is completely eliminated, meanwhile the total dislocation density is reduced.
density is reduced much. Free electron emissions at 3.3774 eV (Xa) and 3.838 eV (Xb) are observed in photoluminescence at 4.2 K further indicating the high quality of the resulting ZnO epilayers.

11:30 AM L4.5
DEFECTS AND STRUCTURE OF INTERFACE IN MgZn$_{1-x}$O/α-Al$_2$O$_3$ HETEROSTRUCTURES. A. Kuri, A.K. Sharma and J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Recently, ZnO has attracted attention not only as a suitable closely lattice-matched substrate for GaN but also as a potentially useful active optoelectronic material itself. This raises new questions not only about the basic properties of ZnO but also about those of related materials that can be alloyed with ZnO in heteroepitaxial structures. One would need a material with a higher band gap to use as barrier in order to make ZnO quantum wells. Recently it was shown that it is possible to grow MgZn$_{1-x}$O alloy films with a wide range of alloy compositions, and in a certain range of alloy concentrations up to 50%. In this work, we report the transmission microscopy study of typical extended defects and microstructural features in the epitaxial hexagonal MgZn$_{1-x}$O$_3$ and Mg$_{1+x}$Zn$_{1-x}$O$_3$ alloy films grown on α-Al$_2$O$_3$ substrate. These layers were synthesized by pulsed laser deposition using ICF excimer laser in high vacuum chamber. The temperature of substrate varies in the range 700-750°C for optimization of growth parameters. The PLD films were found to be single-crystalline structure with high concentration of dislocation up to 10$^{10}$ cm$^{-2}$ at a film thickness 1 μm. The typical structure of defects and interfaces in these films is analyzed and compared with ZnO epitaxial films grown at the same time. It was found a 30° rotation of MgZn$_{0.5}$O$_2$ basal planes with respect to substrate planes is similar to ZnO/Sapphire growth. In contrast to ZnO/Sapphire we do not observe stacking faults in high concentration in MgZn$_{0.5}$O$_2$ epitaxial films. Finally, the evolution of extended defect density with thickness and time of annealing was investigated.

11:45 AM L4.6
EPITAXIAL GROWTH OF Co$_3$O$_4$ THIN FILMS BY LOW TEMPERATURE, LOW PRESSURE MOCVD. K. Shalini, Anil U. Mane, R. Lakshmi, S.A. Shivasankar, Indian Institute of Science, Materials Research Centre, Bangalore, INDIA, M. Rajasekhar, Univ. of Maryland, Dept. of Physics, College Park, MD.

Strongly oriented or epitaxial growth of thin films of metal oxides generally requires relatively high growth temperatures or infusion of gas through means such as ion bombardment during film growth. We have grown epitaxial thin films of the cubic oxide Co$_3$O$_4$ on different substrates at temperatures as low as 450°C by low pressure metalorganic chemical vapor deposition (MOCVD) using a cobalt β-diketonate complex as the CVD precursor and argon as the carrier gas for the sublimed vapors. When oxygen is used as the reactive gas, polycrystalline films of Co$_3$O$_4$ are formed at temperatures ranging from 400-550°C on glass and Si(100) substrates, at a total pressure of about 600 Pa. Under similar conditions, growth of Co$_3$O$_4$ at 450°C, epitaxial films of Co$_3$O$_4$ with [100] orientation are achieved from single crystal SrTiO$_3$(100). A film grown simultaneously on LaAlO$_3$(100) substrate is also epitaxial, having the (100) orientation. The epitaxial growth of the films (out-of-plane texturing and in-plane alignment) was determined by 4-circle x-ray diffraction. The films on SrTiO$_3$(100), as grown, showing rocking FWHM ~ 0.33 degree, which is comparable to the best values in epitaxial perovskite oxide films grown significantly by higher temperatures. The film thicknesses range from 50 to 1000 Å. In an attempt to improve the epitaxy, the films were annealed at 725°C in oxygen. The rocking FWHM of the annealed films improves to 0.29 degree on SrTiO$_3$(100), and to 1.3 degree on LaAlO$_3$(100). On both these substrates, x-ray scan analysis indicates epitaxial in-plane alignment of the films with the substrate for both Co$_3$O$_4$-grown and annealed films. Details of the epitaxial alignment on the two substrates will be presented for the observed low temperature epitaxy will be proposed.

SESSION L5 IN-SITU STUDIES OF OXIDE GROWTH ON SILICON

Chair: Marilyn E. Hawley and Orlando Auciello
Tuesday Afternoon, April 25, 2000
Salon 10/11 (Marriott)

1:30 PM L5.1
STUDIES OF FERROELECTRIC THIN FILM GROWTH AND SURFACE PHYSICS VIA IN SITU ELLIPSOGRAPHY, TIME-OF-FLIGHT ION SCATTERING, AND DIRECT RECOIL SPECTROSCOPY IN WIDE RANGE PRESSURE ENVIRONMENTS. A.R. Krause, A.M. Diotte, Argonne National Laboratory, Materials Science and Chemistry Divisions,
Argonne, IL; O. Auciello, J. Im, Argonne National Laboratory, Materials Science Division, Argonne, IL; E.E. Irene, Y. Gao, A.H. Mueller, Department of Chemistry, University of North Carolina, Chapel Hill, NC; S. Agarwal and R. Ramesh, University of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

The science and technology of ferroelectric and high dielectric constant thin films has experienced an explosive development during the last ten years. Low-density non-volatile ferroelectric random access memories (NVRAM's) are now incorporated in commercial products such as smart cards and cellular phones. In addition, high dielectric constant thin films will be introduced in the near future into DRAMS. However, substantial work remains to be done to develop materials integration strategies for high-density NVRAMs and high performance DRAMS. With these goals demonstrated the implementation of a variety of complimentary in situ or in situ, real-time characterization techniques is critical to understand film growth and post-deposition processes. We have developed a time of flight ion scattering and recoil spectroscopy (TOF-ISARS) technique to perform in situ, real-time studies of film growth processes in a wide range of background pressures from high vacuum to tens of millitorr.

TOF-ISARS involves three distinct but closely related experimental methods, namely: ion scattering spectroscopy (ISS), direct recoil spectroscopy (DRS) and mass spectroscopy of recoiled ions (MSR), which are capable of providing noninvasive specific information on film growth and surface segregation processes in the ambient conditions required for growing ferroelectric and other oxide thin films. TOF-ISARS can monitor the surface composition and structure of thin films, but not buried interfaces. Therefore, we have combined TOF-ISARS with Spectroscopic Ellipsometry, which permits investigation of buried interfaces as they are being formed. Recent work performed to understand growth and post-deposition processes and microstructure-property relationships of layered perovskite SrBi$_2$Ta$_2$O$_9$ (SBT) and Bi$_{1-x}$Ta$_2$O$_5$ (BTO) thin films will be discussed.

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2:00 PM L5.2
IN-SITU REAL-TIME STUDIES OF COMPLEX OXIDE FILMS FOR ELECTRONIC APPLICATIONS. Eugene A. Irene, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC.

Modern electronic materials applications such as MOSFET's require the use complex oxide films for gate dielectrics and storage capacitors in conventional MOSFET's, and as polymerizable media in ferroelectric based MOSFET's. Because of the level of perfection required for these applications, the film deposition processes must be monitored and controlled in terms of the film composition, structure and morphology. Information on process dynamics, in order to reliably obtain the correct film thicknesses. Barrier films will be required which allow reaction of the complex oxide with a variety of substrates and contact material. On the scientific side, the detail of interactions between complex oxide films and substrates are difficult to study because the growing film covers the interface. In order to address all these issues we have developed a world-wide unique deposition and characterization system as a collaboration between UNC, Argonne National Laboratory, ANL and Ionworks Inc. This system comprises a vacuum chamber multi target sputter ion deposition subsystem with spectroscopic ellipsometry (SE) and time of flight ion scattering and recoil spectroscopy (TOF-ISARS). Characterization can be performed. A mechanism for understanding the use of the substrate deposition and annealing processes. In this review this unique system will be briefly discussed, and the most recent results of in situ real-time complex oxide film growth dynamics, interface interactions, film structure, morphology and barrier film stability will be presented. Examples will be presented from silicon, ferroelectric and device contact research areas during the ongoing collaborative studies.

2:30 PM L5.3
IN-SITU STUDY OF BARRIER LAYERS USING SPECTROSCOPIC ELLIPSOGRAPHY AND MASS SPECTROSCOPY OF RECOILED IONS. Y. Gao, A.H. Mueller, E.A. Irene, Department of Chemistry, University of North Carolina, Chapel Hill, NC; O. Auciello, A.R. Krause, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; J.A. Schultz, Ionworks Inc, Houston, TX.

With the miniaturization of modern devices, more complex multilevel
structures are required for the fabrication of electrical contacts, and
different new materials need to integrated into the technology, in
order to optimize device performance. Both the pronounce and
diversity increase the possibility of interdiffusion and/or chemical
reactions between multilayer thin film materials. Barrier films help to
reduce these unwanted interactions. Hence, a rapidly growing
number of studies have been devoted to evaluate the stability and
barrier properties of a wide variety of materials. However, most of
these analysis have been performed with co-sputtered and/or using
destructive techniques, such as Rutherford backscattering spectrometry
(RBS), X-ray diffraction (XRD), Auger electron spectroscopy (AES)
depth profile, transmission electron microscopy [TEM] and electrical measurements. The objective of this study is to
demonstrate in-situ real time methodology to monitor the
evolution of barrier effectiveness. In this paper, it will be shown that
spectroscopic ellipsometry (SE) and diﬀerentially pumped mass
spectroscopy of recoiled ions [MRIS] enables the detection of barrier
layer performance for processing conditions. As examples, we will
present new results of in-situ studies of the interdiffusion and
interaction between Cu/Si with/without a TaSb/Si barrier layer; as
well as the thermal stability study of the barrier layer for BiST high K
dielectric films with Ir electrodes in dynamic random access memory
[DRAM] device structures.

SESSION L6: EPITAXIAL GROWTH OF OXIDES ON SILICON

Chairs: Darrell G. Schlom and Orlando Anciello
Tuesday Afternoon, April 25, 2000
Salon 10/11 (Marrriott)

3:15 PM #6.1 STRUCTURE OF THE SILICON-OXIDE INTERFACE. Yuahi Tu and J. Tamell, IBM,T.J. Watson Research Center, Yorktown Heights, NY.

Interfaces between crystalline and amorphous materials play a crucial role in devices and device fabrication. The most important example is undoubtedly the interface between crystalline Si and its amorphous
native oxide SiO2. This remarkable interface is the basis for most current computer technology, yet its structure remains poorly
understood. We have developed a new computational approach to this
problem, which allows us to compute interface properties of the amorphous oxide. The approach makes possible the first
calculation of equilibrium interface structures and energies for an
amorphous-oxide interface. This talk describes our method, and
presents a model for the Si-SiO2 interface that has low energy and
reconciles a variety of puzzling experimental results.

3:45 PM #6.2 HETEROSTRUCTURE AT AN OXIDE/SEMICONDUCTOR INTERFACE - A CORRELATION BETWEEN PHYSICAL AND ELECTRICAL STRUCTURE. Rodney McKe, Oak Ridge National Laboratory, Oak Ridge, TN.

The fundamental interest in oxide/semiconductor heterostructures primarily reside in developing an understanding of length scale
issues. Chemical bonding and crystal symmetry are overriding current understandings. We present a comprehensive study of the
dissimilar materials and two cases will be discussed in this talk:
BaSrO and SnTeO3 on silicon and BaO and SnTeO3 on germanium.
We will present an experimental study and results in which
common present heteroepitaxy can be obtained in these systems, and
use simple oxide/semiconductor capacitors to demonstrate the
coupling between the physical and electrical structure at the interface.
The utility of such experiments goes directly to the question of
whether an alternative to the SiO2 dielectric on silicon can be
obtained using high performance crystalline oxides. Sponsored by the
Division of Materials Sciences, Office of Basic Energy Sciences, U. S.
Department of Energy under contract DE-AC05-88OR22304 with
Lockheed Martin Energy Research Corporation.

4:15 PM L6.3 METAL-ORGANIC MOLEcular BEAm EPITAXY OF MAGNESCUM CxEx OXIDE ON SILICON. F. Niu, B.H. Hoerman and B.W. Wessels, Dept. of Materials Science and Engineering and
Materials Research Center, Northwestern University, Evanston, IL.

Epitaxial MgO films have been grown on single crystal Si (001)
substrates by metalorganic molecular beam epitaxy using a solid
precursor, magnesium butylidoxalate and activated oxygen. The
process involves the growth of thin epitaxial interlayer followed by
deposition of MgO. The overlayer was epitaxial with a
MgO(001)/Si[001], MgO[110]/Si[110] orientation. The structure of the interlayer and oxide layer was characterized by RHEED and
high-resolution transmission electron microscopy. The composition
was determined by Auger electron spectroscopy and Fourier transform
infrared spectroscopy. The formation of the interlayer and MgO was
studied with RHEED.

4:30 PM PANEL DISCUSSION

SESSION L7: EPITAXY OF OXIDES ON SILICON

Chairs: Jeffrey W. Bullard and Bruce W. Wessels
Wednesday Morning, April 26, 2000
Salon 10/11 (Marrriott)

Motorola Labs, Tempe, AZ.

Epitaxial oxide high k transistors could provide the platform for a
new class of silicon transistors. SiO2 gate oxide scaling is reaching a
physical tunneling limit, and higher dielectric constant materials will
be the gate insulator for future MOSFET devices. SiO2 (STO) appears to
be very promising due to its high dielectric constant and
good insulating properties. Epitaxial oxide devices have not been
practical to produce for a number of reasons, mainly relating to
chemical and electrical problems at the interface between the oxide
material and silicon. Recently, we have grown epitaxial STO directly on
a Si (001) substrate using molecular beam epitaxy. The films show
good interface and electrical properties. In this presentation, the basic
material growth and resulting properties will be presented, along with
modeling and characterization of our proposed interface structure.


Oxides with perovskite crystal structure are important candidates for
ultrathin gate oxides because of their large DC dielectric constant.
When STO is deposited over the right Si, an amorphous non-
stoichiometric interface (1.63X1A thick) is usually formed during the
later stages of growth. This is undesirable, since it reduces the
capacitance. Optical tools such as spectroscopic ellipsometry (SE) can
easily be adapted for in-line or in-situ diagnosis of SiO2 on Si,
therefore understanding the optical properties of such thin films is
important. When we are interested in the properties of thin films, it is
a good idea to start with studying the bulk. Following Jellison, we
measured the dielectric function of bulk SiO2 from 0.74 to 6.1 eV.
We also performed measurements in the infrared and in the vacuum
UV. In comparison with ab initio band structure calculations, we
identify the critical points in the spectrum at 3.78, 4.29, 4.76, and 6.15
eV due to interband transitions from the O (2p) valence band to the
Ti (3d) conduct band. Unlike SiO2 films grown on MgO, which have the same refractive index as bulk STO, our thin SiO2 films on Si have a lower refractive index. Since the films are smooth in
AMT, this cannot be attributed to surface development. Spectroscopic ellipsometry cannot determine thickness and refractive index n
independently for very thin layers, but rather measures an effective
averaging over the amorphous interface and the STO2 film. For film
thicknesses between 160 and 200A, n at 850 nm ranges from 2.1 to 2.2
(compared to 2.4 in the bulk). Thinner films (116-130A) have an even
lower n around 1.9. We propose that the amorphous interface has a
lower effective bulk SiO2 and therefore reduces the effective n with
decreasing film thickness. For process control, one can try to minimize
the interface thickness by maximizing n.

9:15 AM L7.3 TWO STEPPROCESS FOR THE GROWTH OF A THIN LAYER OF SILICON DIOXIDE FOR TUNELLING EFFECT APPLICATIONS. Jorge Pedro, Hugo Aguş, Ehrira Fortunato, Isabel Ferrera, Rodrigo Martins, New Univ. of Lisboa, Fac. of Science and
Technology, Materials Science Dept., CEFIMAT and CEMOP/UnINNOVA, Monte da Caparica, PORTUGAL.

In the SIS (Semiconductor-Insulator-Semiconductor) solar cells the
insulator plays the main role in the device performances. It should be
very thin (below 4 nm thickness) and also compact, to form the
desired tunneling effect between the two semiconductor layers, the
silicon and the semiconductor oxide. The silicon oxide growth method
proposed consists in a two step process. First the silicon wafer is
oxidized in a furnace at a temperature of 500°C, using a mixture of
oxygen and nitrogen gases. This permits a very slow oxidation that
can be easily controlled by the time of oxidation. In spite of this,
ellipsometric measurements of this oxide revealed a poor compact oxide. To improve the compactness of the oxide, we use a second step process and then thin oxidation treatment. This, which under appropriate conditions can lead to the improvement of the compactness of the silicon dioxide film, as revealed by ellipsometric studies. These results, together with SIMS and RBS data, were correlated with the data obtained from the G-V measurements performed aiming to establish the best oxide properties and thickness that lead to the production of cheap and efficient solar cells.

9:30 A.M. L7.4 DEPOSITION OF Co2O3 THIN FILMS WITH [200] PREFERRED ORIENTATION ON Si(100) SUBSTRATE BY RF-MAGNETRON SPUTTERING. Leeun Kim, Jinmo Kim and Donggeun Jung, Dept. of Physics, Sungkyunkwan Univ., Suwon, SOUTH KOREA.

In recent years, Co2O3 has been studied extensively due to its various applications. Because Co2O3 has a cubic crystal structure and the lattice constant of Co2O3 is close to that of Si, many research groups have attempted to grow epitaxial thin films of Co2O3 on Si substrates in order to produce the silica-on-insulator (SOI) structures by deposition methods. In addition, Co2O3 was used as the intermediate layer between the ferroelectric thin film and the Si substrate in a metal-ferroelectric-semiconductor field effect transistor (MFSFET) to prevent the interdiffusion of the ferroelectric material and the Si substrate. For these applications, it is very important to investigate the crystal orientations of Co2O3 thin films deposited on Si substrates. There are many reports on the growth of Co2O3 [111] layers on Si[111] substrates by e-beam evaporation and the laser ablation. These methods are quite difficult to be used in large scale production lines, whereas radio frequency (rf)-magnetron sputtering is widely used in large scale semiconductor processes. There have been few reports on the growth of Co2O3 films with [200] preferred orientation by sputtering on Si[100] substrates, which are used more than Si[111] substrates. In this work, we have investigated the effect of deposition parameters of rf-magnetron sputtering on the crystallinity of Co2O3 thick films on Si[100] substrates. Deposition temperature, rf-power and seed layer deposition time were important parameters affecting the crystallinity of Co2O3 thin films. The Co2O3 [200] peak was notable for a deposition temperature above 600°C. With increased rf-power and thus lower deposition rate, the intensity of the Co2O3 [200] peak increased. With the seed layer deposition time less than 20 sec, the Co2O3 [200] peak dominated. By optimizing these parameters, Co2O3 thin films with a strongly preferred orientation in the [200] direction could be deposited on Si[100] substrates by rf-magnetron sputtering.

SESSION 18: EPITAXY OF OXIDES AND METALS
Chair: Jeffrey W. Bullard and Bruce W. Wessels
Wednesday Morning, April 26, 2000
Salon 10/11 (Marriott)

10:15 A.M. L8.1 IN SITU REAL TIME STUDIES OF OXYGEN INCORPORATION IN COMPLEX OXIDE THIN FILMS USING SPECTROSCOPIC ELLIPSOMETRY AND ION SCATTERING AND RECOIL SPECTROMETRY.

A.H. Mueller, Y. Gao, E.A. Irene, University of North Carolina at Chapel Hill, Dept. of Chemistry, NC. O. A. Krauss, Argonne National Laboratory, Material Science and Chemistry Division, Argonne, IL; J.A. Schatz, Ionwerks, Houston, TX.

The decrease in feature size of electronic devices and the commensurate electronic properties scaling has resulted in a search for new materials to achieve the electronic properties required for such miniaturization. Complex oxide materials have exhibited the necessary properties for use in such technologies as high K DRAM capacitors, Josephson junctions, SQUIDS, and ferroelectric devices. The properties of these films have shown a critical dependence on their oxygen content, such as loss of superconducting transition by YBa2Cu3O7−δ (YBCO) depending upon the exact oxygen content, and the lowering of the dielectric constant of the high K material BaSrTiO3 (BST) under oxygen deprived conditions. The objective of this study is to examine in real time oxygen incorporation and reaction conditions as well as the structural effects using real time, In-Situ Spectroscopic Ellipsometry (SE) and Ion Scattering and Recoil Spectrometry (ISARS). It has been shown that oxygen incorporation into complex oxide thin films can be followed in real time using SE, and the chemical and structural information such as oxygen adsorption and bonding sites may be obtained by the ISARS techniques. These complementary techniques are required in real-time, and as such yield a wealth of information not only about the incorporation of oxygen, but also about the mechanism and structural effects relative to film function. The most recent results YBCO and BST will be presented.

10:30 A.M. L8.2 Mg GROWN ON MgO(001), (011), AND (111) STUDIED BY RHEED AND STM. Guang Chen, Nan-Ji Chen, Jin-Jin Ku, National Chung-Cheng Univ., Dept. of Physics, Chia-Yi, TAIWAN ROC.

Relative to alkali metals, the growth of alkaline earth metals including Mg has not been reported in detail. In this study, Mg film grown on MgO(001), (011) and (111) with high crystalline quality is observed. In situ reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) are used to characterize the surface microstructure during the growth. A pseudomorphic structure of the Mg film is identified by RHEED until the film thickness reaches ~2 mm for all films. This metastable fcc phase is followed by the MgO template even though the close packed midit is ~8%. After the film is thicker than 2 mm, it reduces to hcp but with strong orientational dependence. We observed that it is rather straightforward for a fcc [111] switching to a hcp (001) plane because both planes are close packed. On the other hand, for (011) and (111) there have no corresponded planes in hcp structure. The RHEED diffraction spots of the Mg film before stable patterns with fractional order peaks are observed. We believe that it is related to a fcc-unit cell, which results from a changing of ABCABC (three units of a fcc structure) to ABAB (three units of a hcp structure) layer sequences. Although MgO substrate is highly insulating, a few tens nm thick Mg is able to have tunneling current to get STM images. The morphologies of the thicker film show interesting spiralike, faceting, and terrace modes on the surface similar to (111), (110) and (100) planes, respectively. The orientation dependence of the morphology will be discussed.

10:45 A.M. L8.3 MICROSTRUCTURE AND PROPERTIES OF Bi2Sr2CaCu2O8+ delta THIN FILMS DEPOSITED ON Si SUBSTRATES WITH YSZ BUFFER LAYERS. Qian Wenshaeng, Zhou Xing, School of Electrical & Electronic Engineering, Nanjing Technological University, SINGAPORE; Wei Tong, Micronet Center, Southeast University, Nanjing, PR. CHINA.

Bi2Sr2CaCu2O8+ delta (BSCO) high Tc superconducting films is deposited on Si substrates with YSZ buffer layers by sputtering magnetron sputtering. In growing process, off-axis technique is used to reduce the re-sputtering effect. The technique parameters including deposition temperature, sputtering atmosphere and annealing conditions are optimized. The critical temperature of BSCO film on YSZ/Si is 83K. Scan Electronic Microscope and Atomic Force Microscope are used to observe the surface morphologies of BSCO/YSZ/Si. The spiral grain structure of superconductor grains and the relation between superconducting phases and substrate temperatures are verified. The fractal growth is first found in BSCO/YSZ/Si morphologies. The fractal dimension is 1.795. The geometry and crystal properties of fractal structure are studied. As the result, the fractal formation model in BSCO/YSZ/Si in which diffusion and nucleation exist at the same time is presented and verified. It is also pointed out that the fractal formation appears in the annealing process and has close relation with crystallization of BSCO films. The theoretical analysis of fractal formation mechanism breaks through the unitary diffusion way in DLA and KCA fractal models. This theory is helpful for the improvement of high Tc superconducting films.

11:00 A.M. L8.4 MICROSTRUCTURE AND PROPERTIES OF PbZr0.6Ti0.4O3 AND PbZr0.3Ti0.7O3 THIN FILMS DEPOSITED ON SI OXIDATE LAYERS.

R.E. Kirchmair and M.T. Islam*, Energy Technology Division, Argonne National Laboratory, Argonne, IL; G.R. Bui, Y. Huang and S.K. Streiffer, Materials Science Division, Argonne National Laboratory, Argonne, IL. **Current address: Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Polycrystalline PbZr0.6Ti0.4O3 and PbZr0.3Ti0.7O3 thin films were deposited at 400°C temperatures (450/550°C) on (111)Pt/Ti/SiO2/Si substrates by metal-organic chemical vapor deposition. The film texture could be improved and lower deposition temperatures could be used by depositing the films on Pt/TiOx or TiOx template layers. Films were characterized by scanning tunneling microscopy and by X-ray diffraction; electrical properties were also examined. The microstructure and electrical properties of films deposited on both the original substrate and on the template layers were compared. Based on the results, possible nucleation and growth mechanisms have been proposed. Work supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, under Contract W-31-109-Eng-38.

11:15 A.M. L8.5 SOLUTION SYNTHESIS OF EPITAXIAL RARE-EARTH OXIDE THIN FILMS ON ROLL-TEXTURED NICKEL.

Jonathan S. Morrell, Zhirong B. Xue, University of Tennessee, Knoxville, TN; David B. Beach, Catherine E. Vallet, Mariaspin.
Parranthe, Thomas G. Chinoy, Oak Ridge National Laboratory, Chemical and Materials Science Division, Oak Ridge, TN.

Using solution chemistry, epitaxial films of rare earth oxides of the general formula REO₂₃ (where RE = Sm to Lu) were prepared on cubic-textured nickel tapes. Solutions of metal methoxylates or metal alkoxides with various solvents were used to deposit powders on the nickel substrates. The resulting powders were then compacted into pellets using a die and sintered in a vacuum furnace at 1300°C for 24 hours to form dense, highly textured nickel substrates. These substrates were then coated with the rare earth oxide films using a variety of techniques, including sputtering, evaporation, and chemical bath deposition. The resulting films were characterized using a variety of techniques, including X-ray diffraction, electron microscopy, and spectroscopy.

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SESSION 1: IN-ROOM POSTER SESSION
Wednesday, April 26, 2000
11:15 AM
Salon 10 (Marrriott)

L9.1 STRUCTURE CHARACTERIZATION OF EPITAXIALLY STRAINED YBa₂Cu₃O₇₋ₓ/PrBa₂Cu₃Oₓ: SUPERLATTICES.
M. Varela, Univ Carlos III de Madrid, Dept de Fisica, Leganes, SPAIN. Deigo Arias, Jacobo Santamaria, Univ Complutense de Madrid, Dept de Fisica Aplicada III, Madrid, SPAIN. Carmen Ballesteros, Univ Carlos III de Madrid, Dept de Fisica, Leganes, SPAIN. On leave from Universidad del Quindo, Armenia, COLOMBIA.

The structure of high quality [YBa₂Cu₃O₇₋ₓ/PrBa₂Cu₃Oₓ]₇ nanostructured superlattices is determined using x-ray diffraction and electronic surface probe microscopy. Films were found to be orientated both in the plane and out of the plane of the substrate, free of pinholes and gross defects, and of sufficient quality for use as substrates for high Tc superconductor tape. The microstructure of these films is characterized by the presence of thin epitaxial layers of PrBa₂Cu₃Oₓ which form a superlattice with the YBa₂Cu₃O₇₋ₓ layers. The epitaxial growth of PrBa₂Cu₃Oₓ is enhanced by the presence of a biaxially textured substrate (RABITS) to promote the epitaxial growth of the buffer layer and YBCO coating. Due to the ease of scalable and higher cost efficiency, chemical solution deposition has been investigated as an alternative means of forming both the superconductor and buffer layers. In contrast to physical and chemical vapor deposition techniques, where the nucleation and growth process is dictated by surface and interfacial energy considerations, in solution deposition routes, the nucleation and growth characteristics of the layers are also impacted by the choice of solvents, which can also be chosen to influence the growth rate and quality of the film. In this study, we present the synthesis and characterization of PrBa₂Cu₃Oₓ films grown on YBa₂Cu₃O₇₋ₓ substrates using a chemical solution deposition process. The PrBa₂Cu₃Oₓ layers were grown by spin coating a solution of Pr-acetylacetonate in methanol onto a YBa₂Cu₃O₇₋ₓ substrate. The PrBa₂Cu₃Oₓ layer thickness is controlled by the number of spin coating cycles. The PrBa₂Cu₃Oₓ layers are characterized using x-ray diffraction and electron microscopy. The PrBa₂Cu₃Oₓ layers are found to be epitaxial with the YBa₂Cu₃O₇₋ₓ substrate and have a thickness of 10-20 nm. The PrBa₂Cu₃Oₓ layers are found to be highly textured with a (103) orientation, with a maximum texture of 80% for a PrBa₂Cu₃Oₓ layer thickness of 20 nm. The PrBa₂Cu₃Oₓ layers are found to have a low density of pinholes and small defects.

L9.2 MODELING OF THE TRANSITION FROM ACTIVE TO PASSIVE OXIDATION OF Si(100). Cheol Ho Choi, Mark Gordon, Da-Jong Liu and J.W. Evans, Ames Laboratory, Iowa State University, Ames, IA.

As the temperature is lowered from 1080K to 900K, a transition is observed from active oxidation (etching) to passive oxidation (oxide film growth) of the Si(100) surface when exposed to atomic oxygen [1]. This transition is primarily controlled by the energetics of removal of SiO from the surface. At lower temperatures, the SiO desorption energy is too high for SiO to desorb from the surface, and the Si(100) surface is active. At higher temperatures, the SiO desorption energy is low enough for SiO to desorb from the surface, and the Si(100) surface is passive.

The modeling of this transition involves solving the equations for the adsorption and desorption of SiO on the Si(100) surface. The model includes the effects of temperature, oxygen pressure, and the presence of other gases such as water vapor. The model predicts that the transition from active to passive oxidation occurs at a temperature of 1080K, which is in good agreement with experimental observations. The model also predicts that the transition temperature decreases with increasing oxygen pressure, which is also in good agreement with experimental observations. The model also predicts that the transition temperature increases with increasing water vapor pressure, which is also in good agreement with experimental observations.

L9.3 MICROSCOPICAL STUDY OF THE NUCLEATION AND GROWTH PROCESS OF SOL-GERL DERIVED BUFFER LAYERS FOR THE INTEGRATION OF YBCO ON BIAXILALLY TEXTURED NICKEL. Harold Doblinstein, Robert Schwartz, Clemson Univ, Dept of Ceramic & Materials Engineering, Clemson, SC; Richard Gaeser, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC.

Recently, a promising second generation high temperature superconductor tape product was developed by Oak Ridge National Laboratory. The superconductor tape is fabricated using a biaxially textured substrate (RABITS) to promote the epitaxial growth of the buffer layer and YBCO coating. Due to the ease of scalability and higher cost efficiency, chemical solution deposition has been investigated as an alternative means of forming both the superconductor and buffer layers. In contrast to physical and chemical vapor deposition techniques, where the nucleation and growth process is dictated by surface and interfacial energy considerations, in solution deposition routes, the nucleation and growth characteristics of the layers are also impacted by the choice of solvents, which can also be chosen to influence the nucleation and growth rate. In this study, we present the synthesis and characterization of CeO₂ films grown on MgO substrates using a chemical solution deposition process. The CeO₂ films are grown by spin coating a solution of Ce(III) nitrate in de-ionized water onto a MgO substrate. The CeO₂ films are characterized using x-ray diffraction and electron microscopy. The CeO₂ films are found to be epitaxial with the MgO substrate and have a thickness of 20-30 nm. The CeO₂ films are found to have a low density of pinholes and small defects.

The oxide film is a steady component of metallic titanium and zirconium. The rate of hydrogen transfer through it is one of stages, imposed the limit on the interaction process between monatomic hydrogen and metal, the thin film don't produce a considerable influence on the process of hydrogen adsorption by metal. Activational barriers are conserved for desorptinal flow through the surface film. Thus, film exerts the essentional effect on the processes in a volume, bounded by film. The formation conditions of surface epitaxial films on titanium and zirconium under hydrogen plasma and their influence on the processes of hydrogen phases formation of high pressure at P = 26 Pa have been examined in this paper. Using Auger scanning spectroscopy and electron probe microanalysis the regularities of the thin surface film formation during Ti and Zr hydrogenation in hydrogen plasma have been studied. Their role in hydrogenation is discussed. It has been ascertained that the oxynitride film on zirconium surface in HFDP-plasma is formed in the first moment of hydrogenation and remains unchanged up to the process completion. It is governed by the specimen negative charge as a result of its bombardment with low energy electrons. This potential prevails over oxygen and nitrogen negative potential prevails over oxygen and nitrogen negative potential and prevents from their diffusion into the metal volume. It hinders also from metal cations movement into oxide. The film in this case may grow only when effected by chemical potential. The counterbalancing of potentials leads to the dynamic equilibrium of film growth. This mechanism is valid for the sufficiently thin (~ 0.3-1 μm) oxynitride films. The present mechanism is operated so long as the electrons are capable to overcoming the film barrier. In case of the film thickness exceeding critical one no interaction between atomic hydrogen and metals takes place.